XMaS the **X**-RAY **M**AGNETIC **S**CATTERING
and **H**IGH **R**ESOLUTION **B**EAMLINE *at the*
EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY

Experiment Report Form

This report form is to be filled in by all users or groups of users who have had access to beam time for measurements at the XMaS Beamline.

Reports accompanying requests for additional beam time

An experimental report on previous measurements - if necessary, a preliminary report - must be attached to all subsequent requests for beam time. The Peer Review Panel reserves the right to refuse to examine new proposals from groups who have not reported on the use of beam time allocated previously.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details
- bear in mind that the report will be reduced to 71% of its original size. A type-face such as "Times", 14 points, with a 1.5 line spacing between lines for the text, produces a report which can be read easily.

Deadlines for submission of Experimental Reports

- Within 6 months of the experiment and normally before any subsequent submission

Should you wish to make more general comments on the experiment, please enclose these on a separate sheet, and send both the Report and comments to the XMaS Administrator at the address below.

Published papers

All users must give proper credit to XMaS staff members and proper mention to XMaS facilities which were essential for the results described in any ensuing publication. This should take the following form:

"This work was performed on the EPSRC-funded XMaS beam line at the ESRF, directed by W.G. Stirling and M.J. Cooper. We are grateful to the beam line team of S.D. Brown, D.F. Paul, A. Stunault and P. Thompson for their invaluable assistance, and to S. Beaufoy and J. Kervin for additional support."

Further, they are obliged to send to the XMaS Administrator the complete reference and the abstract of all papers appearing in print, and resulting from the use of the XMaS beamline.

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XMaS the UK-CRG	**Experiment title:** Thickness-dependent crystallisation in thin polymer films	**Experiment number:** **28-01-122**
Beamline: **BM 28**	**Date of experiment:** from: 24 October 2001 to: 30 October 2001	**Date of report:** 10 May 2002
Shifts: 17	**Local contact(s):** David Paul	*Received at XMaS:*

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Report:

Our programme of research into the structure of polymer surfaces has focussed on two systems: poly(ethylene terephthalate) (PET), an archetypal semi-crystalline polymer which is widely used in the production of soft drink bottles, overhead transparencies etc., and poly(dialkyl fluorene) which has rapidly developed over the last two years to be the semiconducting polymer material which is expected to dominate future polymer electronic and optoelectronic devices.

During 1998-99, we concentrated on studying samples in air which had been annealed ex-situ at a range of temperatures. For PET, we observed that crystallisation occurs at the surface for lower annealing temperatures than the bulk of the 1100 Å-thick films. We also found that this surface-induced crystallisation involves strong preferential orientation of the polymer chains with the benzene rings lying parallel to the surface [1].

We constructed a vacuum chamber with a hemispherical beryllium dome for probing the ordering process during in-situ annealing. In June 2000, we performed the first surface diffraction study of in-situ processing of polymers and observed clearly the faster kinetics of ordering at the PET surface (report on experiment SI-573). This was followed by a further study of the kinetics of annealing in PET films and at PET/polystyrene buried interface. We also found evidence that reducing the film thickness to 300 Å partially inhibits crystallisation resulting in behaviour which is more similar to the bulk behaviour in the thicker films.

The aim of this exeriment was to study in detail the effect of layer thickness on surface ordering as the thickness approaches the molecular dimensions. The effect of film thickness on surface ordering has not been investigated previously, but the effect of film thickness on the glass transition temperature T_g has been intensively studied in the last five years or so. In polystyrene T_g is observed to decrease with decreasing film thickness, whereas for poly(methyl methacrylate) T_g can either increase or decrease depending on the strength of interaction with the substrate [2]. Since the chain mobility increases rapidly around T_g,

it is reasonable to expect the onset of crystallisation to be closely linked to T_g. This experiment as therefore aimed to clarify the effect of film thickness and molecular confinement on crystallisation. A second subsidiary aim was to get high quality data that could be fitted in detail to determine the time constants for development of crystalline peaks for the surface and for the bulk so that the detailed kinetics could be quantified and a separate activation energy for crystallisation of the surface and bulk be deduced. This would be a significant step forward in understanding the influence of the surface on polymer crystallisation.

PET films of film thicknesses 1100 Å, 300 Å and 180 Å were spin cast from orthochlorophenol solution, the thicknesses being determined by ellipsometry. In-plane diffraction was obtained at an angle of incidence of 0.16° in order to limit the beam penetration to about 60Å, with a wavelength of 1.60 Å in 16-bunch mode. Time series of scans were taken during *in-situ* annealing for different film thicknesses and annealing temperatures. The in-plane scattering is shown in Fig. 1 for thicknesses of 1100 Å and 180 Å. There is no appreciable difference in crystallisation rate discernable between the two samples.

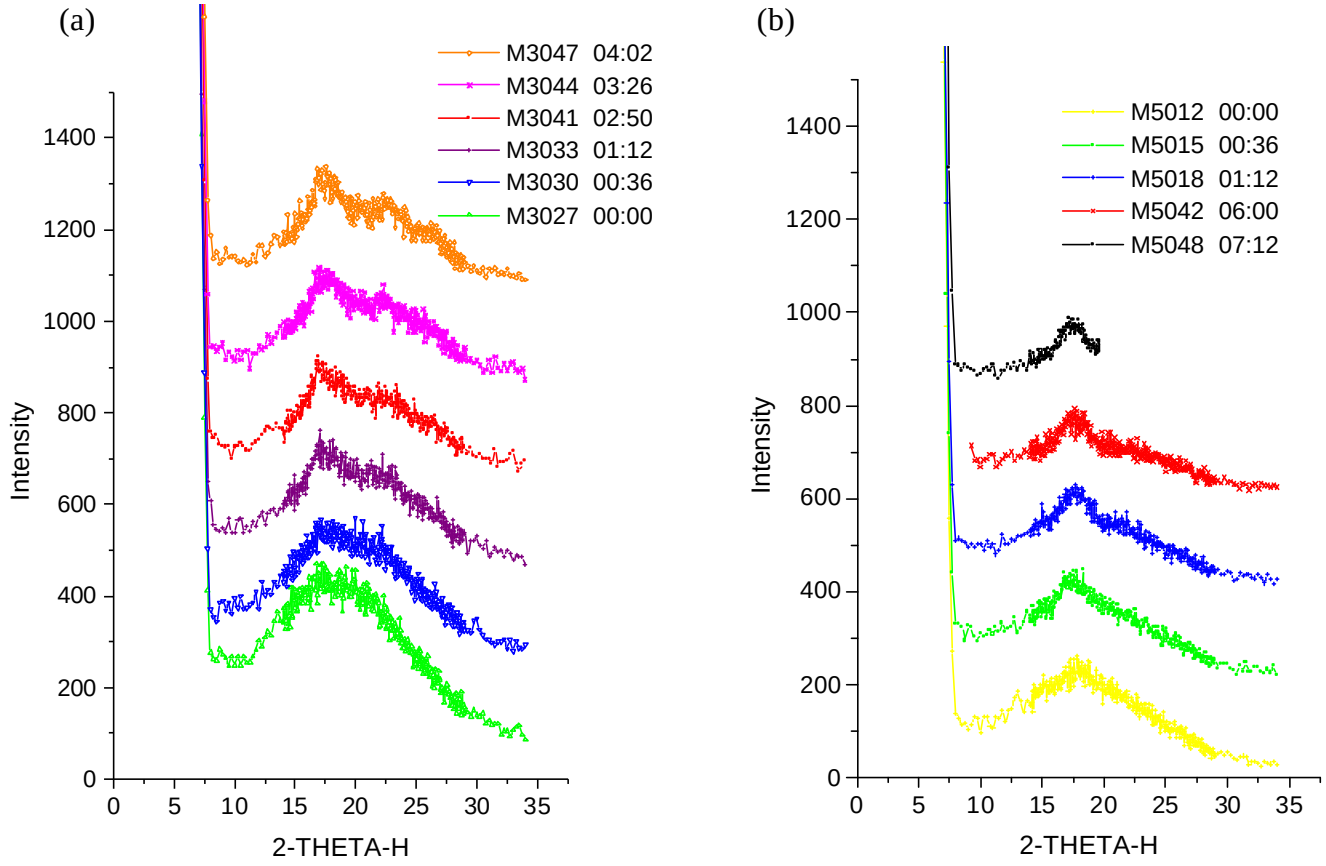

Fig. 1 In-plane diffraction during in-situ annealing of PET films of thichness (a) 1100 Å, (b) 180 Å.

The experiment was hampered by problems with the heating element of the furnace during the first few days of the experiment. During the later stages of the experiment we found that the thermocouple reading 7°C too low whereas the calibration at the start of the experiment showed the temperature measurement to be accurate to <1°C . This degredation which resulted from minor damage during multiple rewiring of the element rendered the data in the second half of the experiment to be untrustworthy. The thickness dependence of the surface crystallisation is now being pursued with *in-situ* annealing studies with AFM in Cardiff.

[1] Surface-induced ordering as a precursor to crystallisation of PET films, M Durrell, J E Macdonald, D Trolley, A Wehrum, P Jukes, R A L Jones, C J Walker and S Brown, Europhysics Letters (2002) in press.

[2] Character of the glass transition in thin supported films, S Kawana and R A L Jones, Physical Review E63 (2001) 021501 and references therein.